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This paper, presented at the 7th American Electroplaters' Society/Environmental Protection Agency Conference on Pollution Control for the Metal Finishing Industry, summarizes present and past metals control research conducted by EPA and presents the approach that EPA is taking to establish standards for Best Demonstrated Available Technology for hazardous wastes.

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HAZARDOUS WASTE RESEARCH PERTAINING TO METAL FINISHING

by Clyde J. Dial

Options for waste management are changing rapidly in the United States. This is true for any industry that produces a hazardous waste. Your industry is no exception. The Environmental Protection Agency (EPA) has conducted research to evaluate or develop metal waste control techniques for a number of years. This paper presents a brief description of the most important projects that have been conducted since 1978. These projects include efforts of the programs that are conducted not only by the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory but also those managed by Roger Wilmoth, Chief of the Manufacturing and Service Industries Branch of the Water Engineering Research Laboratory. Within EPA's research program, these two Laboratories manage all of the engineering research activities of the Agency that deal with hazardous metallic wastes. Work has centered on assessment of the problems and evaluation and development of control techniques or technologies.

Our preference for the management of any waste stream is represented by the following hierarchy:

- Waste elimination,
- Recycle,
- Reuse,
- Burn as fuel,
- Incineration,
- Chemical/biological detoxification,
- Volume reduction, and
- Solidify and dispose.

The current research program is focused on two broad objectives--first, to do performance evaluations of existing treatment technology/waste stream combinations to determine the best demonstrated available technology (BDAT) for that waste stream and, secondly, to explore new concepts that can provide additional options for the control of metals. Work performed by the Office of Solid Waste is providing the analysis from which the technology assessment plan is developed. This report[1] provides an evaluation of the sources and extent of cyanide and metal-bearing hazardous wastes and an analysis of current management practices for treating or disposing of these wastes. It includes an examination of the costs of current practices and the residuals and the emissions from treatment systems. From the 1983 study, the nationwide generation rate of metal-bearing wastes was 7.9 billion gallons per year. The rate of generation of cyanide metal-bearing wastes was 4.7 billion gallons per year, and the estimated rate of generation of reactive wastes containing cyanides was 0.8 billion gallons per year. The greatest number

of waste-generating facilities studied was related to the plating and polishing, paints and allied products, metal coatings and allied products, motor vehicle parts and accessories, and industrial inorganic chemical industries. Wastes handled by treatment, storage and disposal facilities amounted to 5.8 billion gallons of metal-bearing wastes, 3.3 billion gallons of cyanide-bearing wastes, and 0.76 billion gallons of reactive wastes reported as cyanide bearing. Nearly a fourth of all of these wastes were land disposed, and approximately 85 percent of those wastes were aqueous. The most common method for land disposal was deep-well injection. Treatment schemes were identified which will chemically or physically fix these wastes such that their solubility or leachability is well within the California-ban criteria and the EP toxicity criteria.

The Agency's approach to managing hazardous wastes will be to require that the waste stream, after treatment, passes three tests before it may be land disposed. The first test is the "paint filter" test. This is a simple test to ensure that the waste does not contain free moisture prior to placing it in a land disposal operation.

The second test concerns the landfill restriction or BDAT number. For each hazardous component that may be present in a particular listed waste, EPA will establish maximum concentrations that are permissible in order for that waste to be disposed to the land. This maximum concentration will be based on protection of human health and the environment or will represent the lowest concentration that can be achieved through treatment with the BDAT. Work, which will be described shortly, centers on producing these numbers for the Agency.

The third test that must be passed is the proposed toxicity characteristics leaching procedure (TCLP). This TCLP contains a health-based limit for some 54 compounds, including 9 metals. If the leachate found through the TCLP contains concentrations of the TCLP listed compounds in excess of the limits established for the TCLP, the waste must be treated until the waste passes the TCLP.

In order to establish the BDAT, a matrix of control technology processes for waste streams containing metals and cyanides has been developed. The control technology processes under consideration are incineration, sulfate precipitation, alkaline chlorination, chromate reduction, sulfide precipitation, lime precipitation, and solidification/stabilization. For each of these processes, engineering judgment will be used to determine what is considered to be the best treatment train for those metal and cyanide wastes that are being controlled by the Agency under RCRA. There are 66 such wastes. They include five categories:

- D - Wastes because they exhibit a specific characteristic,
- F - Non-specific wastes, regardless of source,
- K - Wastes from specific operations,
- P - Acutely hazardous commercial products or process intermediates, and
- U - Specific commercial products that are toxic.

After having determined what is believed to be the best treatment scheme, actual performance evaluations to demonstrate the type of treatment capability that exists for that waste stream will be conducted. These demonstrations will be done in one of three ways. Actual visits to a facility that is using that treatment scheme for a particular waste will be made, and full-scale performance evaluations of that system will be done. In other cases, mobile pilot-scale equipment will be taken to a field site to use a slip-stream from that facility to demonstrate the treatment capability at pilot scale. Treatment capabilities will also be demonstrated by bringing a particular waste to the Test and Evaluation Facility in Cincinnati to test at pilot scale. As one might suspect, each individual waste stream will not be tested, primarily for two reasons. First, in practice, some of these waste streams are rarely separated from others. Secondly, a number of the waste streams has characteristics almost identical to others, and in those cases, tests of one of the waste streams will be done to demonstrate treatment capability for each of the waste streams in that group having common characteristics.

The evaluation program is under way. So far, performance evaluations have been conducted for the sites listed in Table 1. Because these performance evaluations have just recently been completed, the results of this work are not yet available. This information and information on further planned tests will be available for use on a continuous basis in about two months. It is important to note that the cooperation of industry with the EPA in the conduct of this performance evaluation program has been quite good. This cooperative spirit between the industry and ourselves is essential in order to arrive at the most common sense decisions regarding the management of these metal-bearing wastes.

Currently, two projects that are under way could lead to new techniques to selectively remove metal from waste streams. The first is actually a continuation of the metal recovery program at Montana Tech. This research is aimed at improving the iron removal step of the process. The initial recovery process precipitated the iron as a jarosite, a complex mineral containing iron, potassium, sulfur, oxygen and hydrogen. Although the jarosite forms an easily filterable precipitate, it has the disadvantage of carrying down other cations into its crystalline matrix. Since some of these are toxic heavy metal ions whose concentrations are above those allowed by the RCRA reauthorization, we have had to take a different approach to iron removal.

The current project is based on chemistry whereby the copper is removed first by cementation on iron powder (in previous work copper was removed by solvent extraction after jarosite precipitation) and then iron is precipitated with phosphoric acid. The phosphate thus formed is even easier to filter than the jarosite, and after the iron is precipitated, heating the solution to about 80° Celsius precipitates chromium as the phosphate. This application of phosphate precipitation will be tested to recover metals from mixed metal sludges such as those from plating wastes and electrochemical machining.

A second potentially valuable program is evaluation of compounds which can selectively remove metal from aqueous streams. This effort is the first

TABLE 1

TEST SUMMARIES

LANDFILL BAN PERFORMANCE EVALUATION PROGRAM

SITES TESTED

Waste Codes	Waste Composition	Waste Source	Treatment Technology	Principal Performance Parameters
D002 Spent Nitric Acids and Metals	38% Nitric Acid (E) 5-10% Copper (E) <0.1% Organics (E) 50+% Water (E)	Electronics (Printed Circuit Board Manufacturing)	Neut./Lime Addition/ Precipitation/ Centrifugation/ Reclaimed Metal	Metals, VOC's, pH, TOC, EP tox., TCLP, Paint Filter
D002, D004 Mixed Aqueous Metal-Laden	2% Arsenic (E) 25% Nitric Acid (E) 3% HF (E) 70% Water (E)	Aerospace, Auto Manufacturing	Chemical Coag./ Precipitation/ Sedimentation/ Evaporation/ Carbon Adsorption	TOC, Metals, VOC's, EP tox.
D002, D007, F006 Waste Paint Sludge, Waste Plating Sludge, Cleaning Solution	Paint Sludge (E) Zinc Phos. Sludge (E) Biopond Sludge (E) Metal Sludge (E)	Auto Manufacturing Petroleum Air Force Base	Solidification w/Fly Ash	Paint Filter, EP tox., TCLP
D002 Mixed Aqueous Metal-Laden	<5% Metals (E) <0.1% Organics (E) 95% Water (E) Trace CN (E)	Electrical Components, Applicance Manufacturing	Lime Addition/ Precipitation/ Filtration/ Carbon Adsorption	Metals, VOC's, TOC, EP tox., Cyanide, COD
F007 Cyanide Rinse	<0.5% Metals (E) 500 ppm CN (E) 99% Water (E)	Plating	Cyanide Dest. (alkaline chlorination followed by aqueous waste treatment)	Metals, TOC, CN, VOC's

attempt to use the chemical process that living cells possess that enables them to capture and transfer metals. Their chemical ligands are being synthetically produced for these experiments. Such compositions have, in laboratory demonstrations, removed copper, nickel, and other toxic heavy metals, while letting innocuous ions such as calcium, sodium, etc., pass through. If pilot studies on mixed waste streams, such as leachate from landfills or plating rinse waters are successful, we intend to continue this effort at a larger scale. Our efforts will center on four tasks:

(1) Determine amount of metals removed per gram of compound,

(2) Number of regenerations compound can undergo,

(3) Scale-up so that design and cost estimates may be made (8 to 10 gpm pilot plant), and

(4) Determine effects of organic contaminants on metal removal efficiency.

PAST RESEARCH PROJECTS[2]

The Environmental Protection Agency has sponsored research into metal removal and/or recovery from wastewaters and sludges for over ten years. Early efforts concentrated on precipitating metals to protect waters but the wisdom of also reclaiming metal was soon recognized as a means of reducing water pollution while conserving metal/resources. Work done for EPA at Battelle Columbus in 1975 included a survey of plating facilities and the volume and types of metals discarded in sludges. As understanding of the problem began to develop, a series of investigations was funded, each adding to the overall bank of information. These projects are listed in reverse chronology below.

Metal Value Recovery from Metal Hydroxide Sludges[3]

The latest EPA projects were undertaken at the Montana College of Mineral Science and Technology (Montana Tech) and tied together much of the previous work. The first phase of the investigation was a carefully executed series of laboratory experiments to establish the processes needed to leach hydroxide sludges (the most plentiful type produced by electroplating EP Shops) with sulfuric acid, and the various recovery methods required for copper, zinc, chromium, and nickel. Flowsheets were constructed and the unit operations required to make a complete recovery process were developed.

In phase two, a pilot assembly capable of processing 75-100 lbs. of sludge per day was built and operated at a large electroplating facility. While not entirely troublefree, the operation was smooth enough to allow confirmation of the possible commercial viability of the process, and development of a computerized mass balance.

The steps of the process were as follows.

- The sludge is leached with sulfuric acid.

- Iron, which is frequently present in EP sludges, was removed by precipitating as a potassium jarosite [$KFe_3(SO_4)_2(OH)_6$]. This must be done first, as iron interferes in many of the subsequent recovery steps. This step is in need of improvement, because in the process of precipitating the jarosite some anions such as chromate are removed, along with some heavy metal cations. Even though the volume of the jarosite sludge is much less than that of the starting material, the waste would be classed as hazardous, requiring special precautions and extra costs when landfilling. Because of these faults, it is proposed that a new program be instituted to attempt to remove iron without the inclusion of large amounts of other heavy metals.

- Conventional techniques were used to extract copper from the acid solution using an oxime in petroleum solvent. The copper was then stripped from the organic phase with stronger acid and electrowon or crystallized as sulfate.

- Zinc and cadmium were extracted with diethyl hexyl phosphoric acid (D_2EHPA), leaving chromium and nickel behind. Again, a sulfuric acid strip was used for zinc removal from the organic phase. Small amounts of residual iron are removed in early stages of extraction; ten extraction stages are required to remove iron-free zinc.

- Chromium was oxidized to Cr^{+6} with chlorine, then selectively precipitated as lead chromate which can be sold as a pigment or regenerated to chromic acid with sulfuric acid. The lead sulfate precipitate formed when chromic acid is regenerated may itself be recycled to precipitate more lead chromate. In some instances SO_2/O_2 oxidation of the chromium may be more desirable.

- Nickel is precipitated as sulfide, the only heavy metal in the process which is not directly recyclable back to a plating operation. However, several alternative techniques are presented to yield a nickel ammine, or nickel sulfate may be solvent extracted with a mixture of chelating agents.

Recognizing that some improvements could be made in the various separation steps, first order cost estimates indicate that a 50-ton per day recovery plant could not only reduce landfill volume considerably, with consequent less chance of pollution, but in addition could yield a profit as shown in Table 2.

Metal Recovery from Electrochemical Machining and Electrodischarge Machining (ECM/EDM) Wastes[4]

These relatively new machining processes produce heavy metal wastes; ECM yields hydroxide sludges heavily contaminated with sodium chloride, and EDM finely divided particles of the alloy being machined. Both ECM and EDM are primarily used on hard alloys, often high in nickel, chromium, cobalt, molybdenum, etc. This project involved a survey of ECM/EDM shops, the volumes of sludge

TABLE 2

PROCESS COST: FIRST ORDER ESTIMATE

UNIT OPERATION	COST ($)*			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electro-winning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100
Profit (Gross)			1,071,900	

*Assuming a $1.00 per gallon credit for sludge from producers.

produced, metal content, and disposal practices and costs. Several recovery routes were studied, including the procedures outlined above.

Cadmium Recovery from Electroplating Wastes[5]

This project was primarily concerned with methods and costs for recovering cadmium from plating shops which are able to segregate Cd from other sludges, or perhaps those whose only business is cadmium plating. The authors give very little thought to the fact that many platers use cadmium at least occasionally, and do not segregate their sludges. The recovery technique (melt and/or distill cadmium electromotively displaced with zinc metal) is most effective on low chromium and nickel sludges. While chromium is not displaced by zinc, nickel would have to be removed by distilling the zinc.

Coupled Transport Systems for Control of Heavy Metal Pollutants[6]

Coupled transport membranes are made by immersing a microporous membrane into a liquid complexing agent such as those used for liquid/liquid extraction of metals from solution. The liquid (often called a liquid ion exchanger) then acts as a transfer agent to move metal ions through the capillaries, using the driving force of the pH gradient across a membrane separating an acidic from a basic solution. Data are presented which suggest that a membrane unit having 450 to 500 square feet of surface could separate chromium from the rinse water of a medium sized plating line. The separation unit would cost about $5,000, compared to over $50,000 for an evaporative-ion exchange system.

Evaporative Recovery of Chromium Plating Rinse Waters[7]

A demonstration of this process was given by Advance Plating Company, Cleveland, Ohio on the first of four counterflow rinse tanks. After first passing through a cation exchanger to remove metallic impurities, water from the first rinse tank is drawn into a vacuum evaporator, whose condensate is returned to the third rinse tank. Concentrated acid produced in the evaporator bottoms is returned to the plating bath. The value of recovered chrome has enabled the operator to pay off the equipment in two years or less, in addition, the chromic acid in dragout water is reduced by 99.98%.

Removal of Toxic Metals from Metal Finishing Wastewater by Solvent Extraction[8]

This short investigation of solvent extraction was primarily limited to one extraction agent, Alamine 336 (General Mills). By increasing acidity stepwise with HCl, selective removal of chromium, cadmium, and zinc from wastewaters was demonstrated. Copper and nickel could not be extracted with this reagent; several other high molecular weight amines were tried without success.

Reverse Osmosis Field Test: Treatment of Watts Nickel Rinse Waters[9]

Rinse waters from a Watts type (primarily nickel sulfate) nickel plating operation were passed through a polyamide membrane, effectively separating

a concentrated nickel salt solution and recycling the rinse water. Results were very encouraging, indicating that the capital cost of the R.O. unit could be recovered in about a year, based on the reduction in water usage plus metal values returned to the plating bath. This process could be more accurately described as recycling or conservation since there is no chemical change of metals recycled to the bath.

Treatment of Metal Finishing Wastes by Sulfide Precipitation[10,11,12,13]

Although the process of sulfide precipitation has been known for many years, its use as a means of pollution control appears to be of fairly recent origin, and, is mentioned here primarily to illustrate an effective method of metal removal. A major disadvantage of sulfide precipitation is the lack of selectivity; it is apparently impossible to precipitate a single metal without major contamination by other metal sulfides. Use of a polymeric flocculant (preferably anionic) increased the settling rate, and adding a chelating agent such as EDTA (ethylenediamine tetraacetic) acid at the proper pH greatly aided selectivity.

Heavy metal sulfides, even if effectively separated, are extremely difficult to reduce to their corresponding metals by hydrometallurgical methods, and are generally recovered by smelting. The large volumes of raw material required to support such smelters makes plating waste metal recovery by this method impractical.

A Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges[14]

A survey of plating opertions involving over 600 questionnaires (150 replies) revealed the extent of sludges generated by the industry, and even developed a "typical" analysis of metal content; the copper, nickel, and chromium contents were very similar to those found in subsequent studies. Some preliminary laboratory leaching and extraction studies led to the conclusion that metal recovery could be economically feasible only if the process could be carried out on a large, and preferably continuous scale. Based on then current (1971) metal prices, it was concluded that chromium and zinc recovery were uneconomic; the writers apparently did not foresee the ban on landfilling of heavy metal wastes now being implemented.[12] The only laboratory work done by these investigators were leaching experiments with ammonium carbonate and sulfuric acid which indicated that acid leaches were adequate for most hydroxide sludges while ammonium carbonate would only dissolve copper and nickel. A literature study of several potential recovery methods for copper and nickel was made, but no work was done to verify their efficacy; again, chromium recovery was not considered.

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